

Perfluorinated Polyimide Synthesis

Shinji Ando,* Tohru Matsuura, and Shigekuni Sasaki

NTT Interdisciplinary Research Laboratories, Midori-cho 3-9-11, Musashino-shi, Tokyo 180, Japan

Received April 1, 1992

Revised Manuscript Received August 10, 1992

Polymers are expected to be used as media for transmitting near-infrared light in such optical communication applications as the waveguide in optoelectronic integrated circuits (OEIC) and in multichip interconnections.^{1,2} The current manufacturing process for ICs and multichip modules includes soldering at 260 °C and short-term processes at temperatures of up to 400 °C. Waveguide polymeric materials should therefore have high thermal stability—that is, a high glass transition temperature (T_g) and a high polymer decomposition temperature—as well as high transparency at the wavelengths of optical communication (WOC), 1.0–1.7 μm .

Conventional waveguide polymeric materials, such as poly(methyl methacrylate) (PMMA) or polycarbonates (PC), do not have such thermal stability. In addition, their optical losses at the WOC are much higher than in the visible region (0.4–0.8 μm) because carbon–hydrogen bonds (C–H bonds) harmonically absorb near-infrared radiation. Two or more types of C–H bonds in PMMA and PC—those in methyl, methylene, methyne, and phenyl groups—give strong and multiple absorption peaks at the WOC. Conventional thermally stable polymers like polyimides, on the other hand, have been investigated as optical waveguide materials.^{3–5} It has been reported that optimally cured partially fluorinated polyimides can be used to decrease optical losses below 0.1 dB/cm at 0.63 μm .⁵ As described below, however, partially fluorinated polyimides also have some absorption peaks that originate from the C–H bonds in their phenyl groups.

The substitution of hydrogen atoms by deuterium (D) or fluorine (F) decreases optical losses because the wavelengths of the fundamental stretching vibrations of C–D and C–F bonds are about 1.4 and 2.8 times larger than that of the C–H bond.^{6,7} Low loss waveguides of less than 0.1 dB/cm at 1.3 μm have been fabricated using deuterated or fluorodeuterated PMMA.⁸ Perdeuteration, however, seems inadequate for decreasing optical losses over the entire WOC because the third harmonics of the C–D bond stretching appearing around 1.5 μm ⁹ is not negligible. On the other hand, perfluorinated amorphous polymers, such as Cytop (Asahi Glass Co.), have been reported to have no absorption peaks between 1.0 and 2.5 μm .¹⁰ The combination of low optical losses in the near-infrared region and high thermal stability has therefore to be attained by the perfluorination of polyimides. This study reports the first synthesis of a perfluorinated polyimide.

Because of the high electronegativity of fluorine, the substitution of fluorine for all the hydrogens of aromatic diamines (except for those in amino groups) considerably decreases the reactivity of diamines for acylation. The electron-donating properties, which determine the reactivity for acylation,^{11,12} of five kinds of diamines (shown in Figure 1) were estimated from ¹⁵N and ¹H NMR chemical shifts. Of these five diamines, tetrafluoro-*m*-phenylenediamine (4FMPD) showed the highest reactivity.¹³ Then the only existing perfluorinated dianhydride,¹⁴ 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic di-

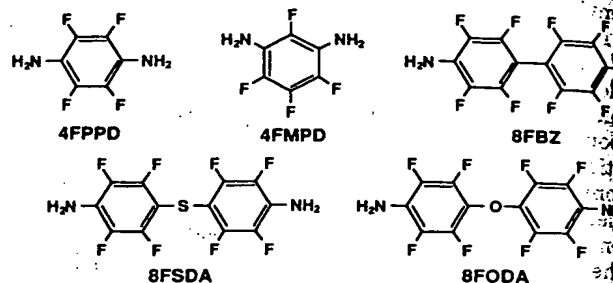
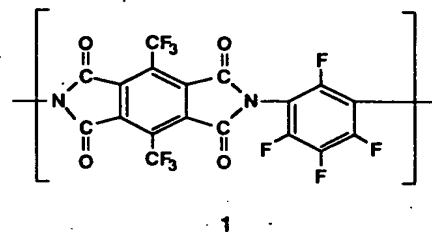


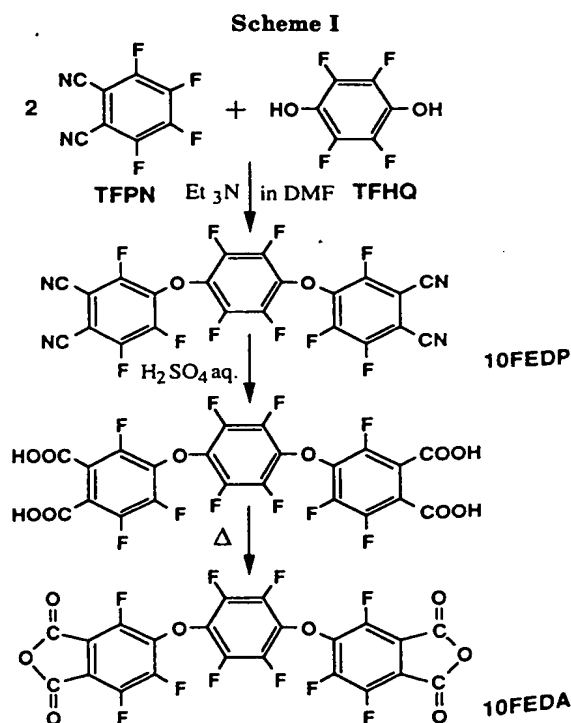
Figure 1. Structures of diamines.

anhydrides (P6FDA), was used to synthesize a perfluorinated polyimide with 4FMPD by the conventional two-step method (same as that described below). The perfluorinated polyimide (P6FDA/4FMPD, structure 1)



was, however, brittle and did not form a continuous film. This was due to the inflexibility of the polymer chain which is ascribed to the absence of linkage groups between ring structures and to the steric interaction between fluorine and the trifluoromethyl group. Because the introduction of fluorine into dianhydrides, on the other hand, increases the reactivity for acylation,¹² tough and flexible films of perfluorinated polyimides are expected to be obtained by combining diamines, which have relatively high reactivities, with dianhydrides, which have flexible molecular structures.

A novel perfluorinated dianhydride, 1,4-bis(3,4-dicarboxytrifluorophenoxy)tetrafluorobenzene dianhydride (10FEDA), was synthesized according to Scheme I. This



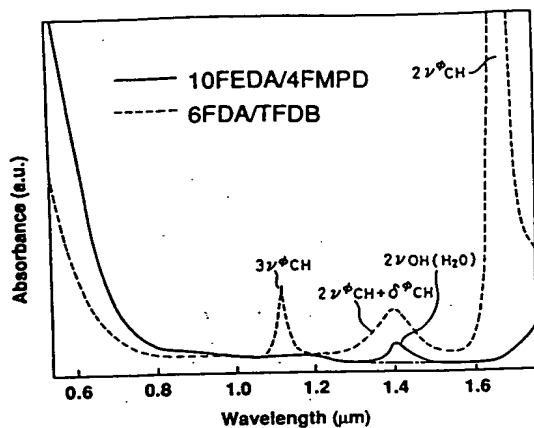


Figure 5. Visible-near-infrared absorption spectra of 10FEDA/4FMPD and 6FDA/TFDB dissolved in acetone- d_6 .

WOC. Partially fluorinated polyimide, on the other hand, has an absorption peak due to the third harmonics of the stretching vibration of the C-H bond ($3\nu^{\text{CH}}$, 1.1 μm), a peak due to the combination of the second harmonics of the stretching vibration and the deformation vibration of the C-H bond ($2\nu^{\text{CH}} + \delta^{\text{CH}}$, 1.4 μm), and a peak due to the second harmonics of the stretching vibration of the C-H bond ($2\nu^{\text{CH}}$, 1.65 μm).

In conclusion, a perfluorinated polyimide that has T_g over 260 $^{\circ}\text{C}$ and a high optical transparency over the entire optical communication wavelengths was synthesized. Their high thermal stability and optical transparency are due to

their fully aromatic molecular structure and the absence of C-H bonds. The use of a diamine, which has a relatively high reactivity, and a new perfluorinated dianhydride, which has a flexible structure, makes it possible to obtain a tough and flexible perfluorinated polyimide film. In addition, this polymer has a low dielectric constant. Perfluorinated polyimides are promising for use as optoelectronic materials.

References and Notes

- (1) Schriever, R.; Franke, H.; Festl, H. G.; Kratzig, E. *Polym.* 1985, 26, 1426.
- (2) Kurokawa, T.; Takato, N.; Katayama, T. *Appl. Opt.* 1980, 19, 3124.
- (3) Franke, H.; Crow, J. D. *SPIE* 1986, 651, 102.
- (4) Sullivan, C. T. *SPIE* 1988, 994, 92.
- (5) Reuter, R.; Franke, H.; Feger, C. *Appl. Opt.* 1988, 27, 456.
- (6) Weeler, O. H. *Chem. Rev.* 1959, 59, 629.
- (7) Schleinitz, H. M. *Wire Cable Symp.* 1977, 25, 352.
- (8) Imamura, S.; Yoshimura, T.; Izawa, T. *Electron. Lett.* 1991, 27, 1342.
- (9) Kaino, T. *Appl. Phys. Lett.* 1986, 48, 757.
- (10) Aozaki, K. *Plastics (Jpn.)* 1991, 42, 51.
- (11) Okude, K.; Miwa, T.; Tochigi, K.; Shimanoki, H. *Polym. Prepr. (Am. Chem. Soc., Div. Chem. Soc.)* 1991, 32, 61.
- (12) Ando, S.; Matsuura, T.; Sasaki, S. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
- (13) Ando, S.; Matsuura, T.; Sasaki, S. *Polym. Prepr. Jpn.* 1991, 40, 828.
- (14) Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromolecules* 1992, 25, 3540.
- (15) Ando, S.; Matsuura, T.; Sasaki, S. *Polymer* 1992, 33, 2934.
- (16) Matsuura, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* 1991, 24, 5001.